Letters to the Editor

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VIBRATIONAL SPECTRA OF THE THREE ISOMERIC TOLUALDEHYDES

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The electronic absorption spectra of *o*-, *m*- and *p*-tolualdehydes in solution and vapour were first reported by Purvis (1914), but he has given only regions of absorption. Recently we have investigated the $\pi-\pi^*$ electronic absorption spectra of these compounds in vapour phase (Singh and Singh, 1966). Raman spectra of these isomers have been recorded by Bonino and Manzoni (1934) and Kahovec and Kohlrausch (1937). However, complete vibrational assignments of these isomers do not seem to have been made. We have, therefore, recorded the infrared absorption spectra of these isomers in liquid phase in the region 400-4600 cm^{-1} and taking into consideration the Raman spectral data for these compounds, have proposed assignments for the observed frequencies.

The chemicals used were manufactured by Fluka Company. These were of pure quality and were used without further purification.

The infrared absorption spectra were recorded in the region 400-750 cm^{-1} on a Perkin-Elmer double beam infrared spectrophotometer (Model 21) with KBr prism using a 0.10 mm. cell and in the region 700-4600 cm^{-1} on a Perkin-Elmer double beam spectrophotometer (Model 13U) with NaCl prism using a 0.05 mm. cell. The accuracy of measurements is 2 cm^{-1} between 400-1500 cm^{-1}, 5cm^{-1} between 1500-3000 cm^{-1} and 10 cm^{-1} above 3000 cm^{-1}.

As an approximation we may assume the CH_3 group to behave as a single particle and the CHO group to lie in the plane of the ring, then the molecule *p*-tolualdehyde would belong to the point group C_{2v}, whereas both *o*- and *m*-tolualdehydes would have C_s symmetry.

The choice of fundamental frequencies is based on general correlation with the spectra of toluene (Wilmshurst and Bernstein, 1957), fluoro-xylenes (Padhye

and Varadarajan, 1959), bromobenzaldehydes (Singh and Singh, 1967) and chlorobenzaldehydes (Padhye and Viladkar, 1960). In making the assignments only relative intensities of Raman and infrared spectra of tolualdehydes have been considered because the polarization measurements of Raman line are not available.

The assignments of all the fundamental frequencies of the three isomeric tolualdehydes have been given in table 1.

Table 1

Correlation of the vibrational frequencies of *o*-, *m*- and *p*-Tolualdehydes in liquid phase

o-Tolualdehyde		*m*-Tolualdehyde		*p*-Tolualdehyde		Assigned mode of vibration
cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	
3066	(2)	3058	(2)	3080	(2)	C—H stretching
3052	(7)	3020	(7)	3040	(8)	C—H stretching
2974	(8)	2938	(8)	2950	(8)	C—H asym. stretching (in methyl group)
2925	(1)			2936	(8)	C—H asy. stretching (in methyl group)
2882	(9)	2838	(9)	2837	(9)	C—H sym. stretching (in methyl group)
2763	(8½)	2846	(8)	2746	(8½)	C—H stretching (in CHO group)
1701	(10)	1701	(10)	1700	(10)	C = O stretching
1610	(9)	1603	(10)	1614	(10)	C = C stretching
1587	(9)	1581	(4)	1514	(5)	C = C stretching
1490	(9)	1481	(3)	1450	(9)	C = C stretching
1459	(7½)	1456	(1)			C—H asym. bending (in methyl group)
1444	(7½)	1442	(sh)	1422	(6)	C—H asym. bending (in methyl group)
1411	(8½)	1392	(9½)	1392	(9)	C — C stretching
1385	(8½)	1360	(8)	1380	(8b)	C—H sym. bending (in methyl group)
1290	(9)	1295	(9½)	1308	(9½)	C—H i.p. bending (in CHO group)
1198	(6)	1247	(10)	1209	(10)	C—H i.p. bending
1162	(8)	1158	(9½)	1170	(10)	C—H i.p. bending
1125	(7)	1146	(9½)	1110	(8)	C—H i.p. bending
1106	(6)	1090	(7)	1018	(6)	C—H i.p. bending
1068	(5)	1044	(6)	1070	(3)	CH_3 rocking
1040	(6)	1008	(6)	1041	(7)	C—C stretching (breathing vibration)

Table 1 (*contd.*)

o-Tolualdehyde		*m*-Tolualdehyde		*p*-Tolualdehyde		Assigned mode of vibration
cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	
967	(4)	965	(sh)	996	(1)	C—H l.p. bending
950	(2)	931	(7½)	952	(2½)	C—H o.p. bending
863	(9½)	894	(6)			C—H o.p. bending
833	(9)	846	(2)	846	(9½)	C—CHO stretching
783	(9)	780	(10)	808	(10b)	C—H l.p. bending
735	(10)	738	(9)	756	(9½)	C—CH_3 stretching
709	(9½)	704	(9)	706	(6½)	CH_3 wagging
660	(10)	687	(9)	693	(3½)	C—C—C o.p. bending
635	(10)	653	(8)	639	(8½)	C—C—C i.p. bending
537	(8)	518	(8½)	601	(10)	C—CH_3 i.p. bending
471	(9½)	444	(8)	483	(10b)	C—C—C i.p. bending
435*	(10)	405	(6)	409	(8)	C—C—C i.p. bending
372*	(0)	341*	(1)	347*	(½)	C—CH_3 i.p. bending
253*	(2)	220*	(2)	210*	(2)	C—CHO i.p. bending
173*	(0)	196*	(2)	188*	(2)	C—CH_3 twisting
		127*	(3)			C—CHO twisting ?

*These values are taken from Raman data.
b = broad, d = diffuse, bd = broad diffuse, sh = shoulder,
i.p. = in-plane, o.p. = out-of-plane, sym. = symmetric and
asym = asymmetric.

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